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**Mail Stop PROVISIONAL PATENT APPLICATION**  
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**P.O. Box 1450**  
**Alexandria, VA 22313-1450**

**TRANSMITTAL OF PROVISIONAL APPLICATION**  
**PURSUANT TO 37 CFR § 1.53(c)**

Application of: David Jarus and Jeffrey A. Cicerchi

whose address is: 33587 Walker Road, Avon Lake, Ohio 44012 USA

For: Nanoclay-Containing Composites and Methods of Making Them

1. Enclosed is a new provisional patent application. It includes 20 pages of text and 0 page(s) of drawings.
2. Please charge Deposit Account No. 07-1077 in the amount of \$160.00 for the fee pursuant to 37 CFR § 1.16(k). Please credit or debit that account as needed to complete the filing of the application.
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**CERTIFICATE OF EXPRESS MAILING**

Under 37 CFR § 1.10, I certify that this application is being deposited, on the date indicated below, with the United States Postal Service "Express Mail Post Office to Addressee" service addressed to the Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450

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## Nanoclay-Containing Composites and Methods of Making Them

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### Field of Invention

This application relates to polymer mixtures containing nanoclays.

### Background of the Invention

10 Nanotechnology is an exciting new field of science. The use of intercalated phyllosilicates, also called smectite clays, particularly montmorillonite clays, has been recognized as valuable for reinforcing fillers.

15 Nanocor, Inc. is a leader in the field of making and selling montmorillonite nanoclays and concentrates of them where the clays are exfoliated. Further technical and commercial information can be found at [www.nanocor.com](http://www.nanocor.com). U.S. Pat. No. 6,632,868 (Qian et al.) discloses intercalates formed with polypropylene/maleic anhydride-modified polypropylene intercalants.

20 One of the polymers into which montmorillonite nanoclay is added is a thermoplastic polyolefin (TPO), particularly where the polyolefin is polypropylene (PP).

### Summary of the Invention

25 For purposes of this invention, "nanocomposite" means mixture comprising thermoplastic matrix polymer and intercalated nanoclay, whether to be used as a concentrate or as a compound. Optionally, but preferably, the nanocomposite contains a compatibilizing dispersion agent, such as maleated polyolefin. Optionally, but preferably, the nanocomposite contains a polyolefin elastomer to enhance impact resistance.

One aspect of the invention is a nanocomposite having a weight ratio of nanoclay to compatibilizing dispersion agent of less than 2.2:1 and greater than 1:1.9. In this ratio, this nanocomposite is useful as a compound for final article formation via molding or extrusion. Preferably, this nanocomposite has a

5 minimum of 9 weight percent nanoclay dispersed in the nanocomposite compound. More preferably, the nanoclay concentration is 10 or more weight percent. Most preferably, the nanoclay concentration is at least 12 weight percent. At 12 weight percent for nanoclay, the amount of compatibilizing dispersion agent is greater than about 5.5 weight percent and less than 22.8

10 weight percent.

Another aspect of the invention is a nanocomposite having a weight ratio of nanoclay to compatibilizing dispersion agent of greater than 3.1:1 and less than 10:1. More preferably, the weight ratio is between about 3.5:1 and 5:1. This nanocomposite is useful as a concentrate for later dilution or "let-down" into polymer or as a final compound for extrusion-grade thermoplastic polyolefins.

Another aspect of this invention is a nanocomposite containing a polyolefin elastomer.

Another aspect of the present invention is a method of making

20 nanocomposite wherein the polyolefin elastomer is added downstream in an extruder from where the other ingredients are added.

Another aspect of the present invention is a method of making

25 nanocomposite compound wherein the thermoplastic matrix polymer, nanoclay, compatibilizing dispersion agent, and optional additives are added as individual ingredients at the inlet of an extruder, followed by addition of polyolefin elastomer (for impact modification) at a downstream port of the extruder. In this manner the TPO is made from all raw materials, not a concentrate of either TPO or nanocomposite.

An advantage of the present invention is that a balance of stiffness and

30 toughness is achieved using in a TPO using the nanocomposites of the present

invention prepared according to the method of the present invention. This balance of stiffness and toughness is superior to those of the TPO without nanoclays therein.

Another advantage of the present invention is that the method delays 5 addition of the optional polyolefin elastomer until after the nanoclay is thoroughly dispersed in the matrix polymer, usually PP. The optional compatibilizing dispersion agent, especially maleated polyolefin, enhances thorough dispersion of the nanoclay in the matrix polymer before any interaction of optional polyolefin elastomer can occur. This delay, it is 10 believed, assures that the nanoclay present is not as likely to become intermixed within the dispersed phase of polyolefin elastomer. Thus, the valuable nanoclay can increase the benefit of its properties in the final article molded from a combination of TPO and the nanocomposite of the present invention.

15 Embodiments of the Invention

TPO's are commercially available from such multi-national sources as Basell Polyolefins. TPO's can have a variety of properties, ranging from rigid to flexible to impact-modified polyolefin copolymers along a continuum known to those skilled in the art. The final use of an article made from TPO benefits 20 from these tailored properties.

The thermoplastic matrix polymer for the present invention can be any thermoplastic suitable for molding or extruding operations where lightness, stiffness, and toughness are desired as performance properties. Non-limiting examples of such polymers are polyolefins, polyamides, polyesters, 25 polyurethanes, styrenic polymers, polycarbonates, polyvinyl halides, and combinations thereof.

Nanoclay is a clay from the smectite family. Smectites have a unique morphology, featuring one dimension in the nanometer range. Montmorillonite clay is the most common member of the smectite clay family. The 30 montmorillonite clay particle is often called a platelet, meaning a sheet-like

structure where the dimensions in two directions far exceed the particle's thickness.

Nanoclay becomes commercially significant if intercalated with an intercalant. An intercalate is a clay-chemical complex wherein the clay gallery spacing has increased, due to the process of surface modification by an intercalant. Under the proper conditions of temperature and shear, an intercalate is capable of exfoliating in a resin matrix. An intercalant is an organic or semi-organic chemical capable of entering the montmorillonite clay gallery and bonding to the surface. Exfoliation describes a dispersion of a surface treated nanoclay in a plastic matrix.

In exfoliated form, nanoclay platelets have a flexible sheet-type structure which is remarkable for its very small size, especially the thickness of the sheet. The length and breadth of the particles range from 1.5  $\mu\text{m}$  down to a few tenths of a micrometer. However, the thickness is astoundingly small, measuring only about a nanometer (a billionth of a meter). These dimensions result in extremely high average aspect ratios (75-500). Moreover, the minuscule size and thickness mean that a single gram contains over a million individual particles.

As defined above, nanocomposites are the combination of the surface treated nanoclay and the plastic matrix. In polymer compounding, a nanocomposite concentrate is a very convenient means of delivery of the nanoclay into the ultimate compound, provided that the plastic matrix of the nanocomposite concentrate is compatible with the principal polymer resin components of the compounds. In such manner, nanocomposites are available in concentrates, masterbatches, and compounds from Nanocor, Inc. of Arlington Heights, Illinois ([www.nanocor.com](http://www.nanocor.com)) and PolyOne Corporation of Avon Lake, Ohio ([www.polyone.com](http://www.polyone.com)) in a variety of nanocomposites.

Nanocomposites offer flame-retardancy properties because such nanocomposite formulations burn at a noticeably reduced burning rate and a hard char forms on the surface. They also exhibit minimum dripping and fire

sparkling.

When using Nanocor produced nanoclay, the amount of this additive in concentrate form can range from about 2 weight percent to about 50 weight percent, and preferably between about 3 and about 40 weight percent of the 5 total compound. Upon addition to the compound, the intercalated nanoclay exfoliates with the addition of compatibilizers known to those skilled in the art. In a preferred embodiment, the compatibilizer is a grafted maleic anhydride such as disclosed in U.S. Pat. No. 5,717,500 (Karande et al.). The use of 10 compatibilizer is also disclosed in U.S. Pat. No. 6,632,868 (Qian et al.), which disclosure is incorporated by reference herein as if rewritten. However the use of "nanocomposite" as defined herein supercedes any inconsistent connotation 15 of that word in Qian et al.

The preparation of nanocomposites uses extrusion mixing equipment known to those skilled in the art, such as disclosed in Qian et al. But the present 15 invention departs from convention. Conventionally, a concentrate is made by mixing TPO and nanoclay, and optionally a compatibilizing dispersion agent such as maleated polypropylene (PP-g-MAH).

In the present invention, the TPO is not used in forming the concentrate. Rather, the constituents of the TPO, (i.e., PP and an elastomer, particularly a 20 polyolefin elastomer), are added separately and at different locations in the extruder. More specifically, the polyolefin elastomer is added downstream of the other ingredients, which gives the nanoclay and its optional dispersion agent both more time and less interference in dispersing completely within the polypropylene carrier. This method of the present invention is useful for 25 making both nanocomposite concentrates and nanocomposite compounds of any weight ratio, including those disclosed in Qian et al.

Preferably, the method of the present invention can be used for concentrates and extrusion-grade compounds where the weight ratio of nanoclay to compatibilizing dispersion agent is greater than 3.1:1 and less than 30 10:1. Preferably, the weight ratio is a range of about 3.1:1 to 5:1.

Also preferably, the method of the present invention can be used for compounds where the weight ratio of nanoclay to compatibilizing dispersion agent of less than 2.2:1 and greater than 1:1.9. Preferably, the weight ratio can be about 1.5:1 to 1:1 and more preferably about 1.33:1 in order to improve both 5 dispersion of nanoclay in the compound (before optional polyolefin elastomer addition downstream of the extruder inlet) and increase the lightness and stiffness of the compound by maximizing the amount of nanoclay that can be dispersed into the compound.

Preferably, the mixing equipment is a co-rotating twin-screw extruder 10 commercially available from Werner-Pfleiderer. The extruder should be capable of screw speeds ranging from about 50 to about 2,000 rpm. The temperature profile from the barrel number two to the die should range from the melting temperature of the thermoplastic matrix polymer to about 270°C, and preferably from around 200°C for this nanoconcentrate. The nanocomposite can 15 be pelletized for later use.

If the weight ratio of nanoclay to compatibilizing dispersion agent is greater than 3.1:1 and less than 10:1, then the pellets are suitable for use as 20 concentrates for dilution or "let-down" in later molding operations to make a final article. Preferably, the concentrate pellets can be added at the inlet of the final molding equipment. Alternatively, the pellets can be used as a compound for certain extruded articles, without further dilution. It has been found 25 unexpectedly that the final balance of mechanical properties desired for the final article can be achieved with a ratio of nanoclay to compatibilizing dispersion agent that minimizes use of that latter material. Thus, the weight ratio is within the range of a nanocomposite concentrate but can be used as a nanocomposite compound, according to the present invention. If the weight ratio of nanoclay to compatibilizing dispersion agent of less than 2.2:1 and greater than 1:1.9, then the pellets are suitable for use as a final compound for molding or extrusion into a final article.

Polyolefin elastomers or rubber in the present invention optionally are used for the separate mixing reason described above, instead of an already blended TPO. Any suitable polyolefin elastomer can be used. For example, polybutadiene rubber, ethylene-propylene-diene rubber (EPDM), ethylene-  
5 octene copolymers, and other elastomers are useful. Non-limiting examples of such elastomers are those commercially available from multinational companies such as Bayer, Dupont-Dow Elastomers, Uniroyal Chemical, ExxonMobil, and others. ENGAGE™ 8180, ENGAGE™ 8842, and other ENGAGE™ polyolefin elastomers are especially preferred ethylene-octene copolymers  
10 available from DuPont Dow Elastomers LLC of Wilmington, DE that function well as impact modifiers for nanocomposites of the invention.

Nanocomposite concentrate pellets of the present invention can be mixed with TPO's to form articles benefiting from a balance of stiffness and toughness properties introduced by the nanoclays therein. The nanocomposite concentrate can be diluted or "let-down" in any ratio that one skilled in the art desires to yield as a final nanoclay concentration in the article.  
15

One way of dilution is with a twin-screw extruder from any number of sources or a continuous mixer from Farrel. Further information on this technique is found at [www.nanocor.com/tech\\_sheets/P806.pdf](http://www.nanocor.com/tech_sheets/P806.pdf) which describes  
20 let-down of conventional nanoconcentrates into TPO's.

Another way of dilution is mixing the nanocomposite concentrate pellets at the point of molding the final article. The mixing inlet for any type of molding machine can be sufficient to disperse the concentrate of the present invention into the TPO. This is an efficient way to introduce a more expensive  
25 concentrate into a final molded product, based on working capital requirements of raw material inventory, because the concentrate arrives just-in-time.

A TPO compounder that does not need to use a concentrate additive for TPO production can add all of the raw materials, except for polyolefin elastomer, at the inlet throat of the extruder. The polyolefin elastomer, to  
30 modify impact and add toughness to the compound, is added at a downstream

port after the nanoclay and compatibilizing dispersion agent have fully intermixed and dispersed into the thermoplastic polyolefin matrix polymer. In this fashion, if the compounder delays the conventional addition of polyolefin elastomer to a mid-extruder location and mixes nanoclay and compatibilizing 5 dispersion agent to the inlet throat of the extruder, that compounder can have all of the processing and performance benefits of a TPO with the added lightness and stiffness provided by the nanoclay therein.

Other Optional Ingredients

10 Those skilled in the art of compounding TPO's recognize the desire to add optional ingredients to the nanocomposites of the present invention. Such optional ingredients include colorants (dyes or pigments), nucleators, blowing agents, activators which lower the activation temperature of the blowing agent, surfactants, plasticizers, stabilizers, flame retardants, UV absorbers, fillers, 15 fragrances, mold release aids, processing aids, biocides, antistatic additives, anti-microbial agents, lubricants, and combinations of them. The optional additives should be added in an effective but not wasteful amount according to the particular processing or performance purposes of such additives in the nanocomposites of the present invention. Without undue experimentation, one 20 skilled in the art can determine the minimum effective amount and the maximum non-wasteful amount for each desired additive.

Usefulness of the Invention

Final molded articles made from TPO are more valuable because 25 nanoclays provide increased lightness and stiffness while retaining toughness. Such molded articles can be made into any number of shapes, among them, automobile parts, large appliance parts, and the like.

Further explanation of the invention is found in the following examples.

30 Examples

Examples 1-17 and Comparative Examples A-C

Nanoclay-containing composites were prepared according to the recipes and commercial sources stated in Table 1 and the mixing conditions stated in Table 2. The concentration of nanoclay and dispersion agent were kept constant with the concentration of polyolefin copolymer rubber being varied.

<b>Table 1</b> <b>Concentrate Recipes for Use in TPO</b>				
<b>Ingredient Wt. %</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Nanoclay	40	40	40	40
PP-g-MAH	10	10	10	10
EO Copolymer Rubber	15	10	5	0
PP	35	40	45	50

  

<b>Commercial Sources</b>		
<b>Ingredient and Use</b>	<b>Source</b>	<b>Brand(s)</b>
Nanoclay to enhance stiffness	Nanocor	I44P
Ethylene-Octene Copolymer to modify impact	DuPont-Dow	EG8180
PP-g-MAH (maleated polypropylene) to disperse nanoclay	Crompton	PolyBond PBX5104
PP (polypropylene) to serve as concentrate carrier		
TPO (thermoplastic polyolefin)	Basell	CA387; Adflex KS311P; and Pro-Fax SG702

The weight ratio of nanoclay to compatibilizing dispersion agent is 4:1, suitable for use as a nanocomposite concentrate.

10

<b>Table 2</b> <b>Concentrate Making Conditions</b>				
<b>Example</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Concentrate Mixing Equipment	Werner & Pfeiderer ZSK 25 co-rotating twin screw extruder			
Concentrate Mixing Temperature	200°C			
Concentrate Mixing Speed	1100 rpm			
Order of Addition	All Ingredients except Ethylene-Octene Copolymer are added together, with EO Copolymer added downstream, i.e., after thorough dispersion of nanoclay and dispersion agent in carrier			

After the concentrates 1-4 were made, they were mixed into three different TPO's to simulate the addition of a nanocomposite concentrate just prior to molding of the TPO into a useful article.

Table 3 shows the amount of dilution, also known as let-down, along 5 with the test results for stiffness and toughness of the final article.

Table 3 TPO Compounds						
Example	Concentrate	Wt. Percent	TPO		Wt. Percent	
Comp. A	--	--	CA387P		100%	
5	1	20%	CA387P		80%	
6	2	20%	CA387P		80%	
7	3	20%	CA387P		80%	
8	4	20%	CA387P		80%	
Comp. B	--	--	Pro-Fax SG702		100%	
9	1	20%	Pro-Fax SG702		80%	
10	2	20%	Pro-Fax SG702		80%	
11	3	20%	Pro-Fax SG702		80%	
12	4	20%	Pro-Fax SG702		80%	
Comp. C	--	--	Adflex KS311P		100%	
13	1	20%	Adflex KS311P		80%	
14	2	20%	Adflex KS311P		80%	
15	3	20%	Adflex KS311P		80%	
16	4	20%	Adflex KS311P		80%	
17	2	10%	Adflex KS311P		90%	

  

Example	ASTM D790 (PSI)		ASTM D3837 (Joules)					
	Flex. Mod.	Stress at Yield	Inst. Impact Room Temp. Peak	Inst. Impact Room Temp. Total	Inst. Impact 0°C Peak	Inst. Impact 0°C Total	Inst. Impact -30°C Peak	Inst. Impact -30°C Total
Comp. A	120000	3380	16.7	30.7			24.9	45
5	149000	3540	16.8	30.5			24.6	39.3
6	157000	3740	16.6	30.2			22.6	27
7	158000	3850	16.6	29.7			13.8	14.4
8	179000	4110	16.5	28.7			3.9	4.9
Comp. B	155000	4770	18.8	33.8	22.4	41.3		
9	233000	5530	20.1	31.1	24.1	37.4		
10	239000	5650	21.1	30.3	18.5	22.5		
11	244000	5720	20.6	28.5				
12	258000	5980	20.6	24.3	11.5	12.1		
Comp. C	78400	2530	13.8	25				
13	123000	3040	16.1	26.9				
14	130000	3220	15.7	26.4				
15	133000	3330	15.1	26.2				
16	149000	3540	15.4	25.4				
17	109000	3010	15.2	26.4				

Table 3 shows that Examples 5-8, 9-12, and 13-16 (each containing 8 wt. percent nanoclay) consistently outperform the Comparative Examples A, B, and C, respectively, in respect of Flexural Modulus and Stress at Yield.

Because each of the Comparative Examples are different types of TPO (A is a rigid TPO; B is an impact copolymer; and C is a flexible TPO), assessment of instrument impact performance is more complex. All of Examples 5-16 exhibit ductility by comparing the peak vs. total instrument impact values. As polyolefin copolymer content decreases, instrument impact performance at the various operational temperatures also decreases. Therefore, the balance of stiffness and toughness is found preferably in Examples 5, 9, and 13.

Examples 14 and 17 compare the amount of nanoclay present in the TPO Compounds of the same ingredients, with Example 14 containing 8% nanoclay and Example 17 containing 4%. Along with Comparative Example C, a trend line can be established from 0 to 4 to 8 weight percent, with increased stiffness along that line.

Examples 18-34 and Comparative Examples D-F

A second set of experiments was conducted to further elucidate the scope of the present invention in the ability to make a final compound directly by introducing the various ingredients as raw materials directly into the extruder. Table 4 shows the ingredients and their commercial sources. Table 5 shows the 7 different recipes (A-G) based on three different formulations and variations of mixing in the extruder. Table 6 shows the results of 20 different extrusions and resulting properties (Examples 18-34 and Comparative Examples D-F). The weight ratio of nanoclay to compatibilizing dispersion agent for all Examples is 12:9 or 1.33:1.

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<b>Table 4</b> <b>Commercial Sources</b>		
<b>Ingredient and Use</b>	<b>Source</b>	<b>Brand(s)</b>
Nanoclay to enhance stiffness	Nanocor	I44P
Ethylene-Octene Copolymer to modify impact	DuPont-Dow	EG8180
PP-g-MAH (maleated polypropylene) to disperse nanoclay	Crompton	PolyBond PBX5104
Polypropylene (12 Melt Flow Index)	Basell	Pro-Fax 6323
Blend of Irganox 1010 and Irgafos 168 Processing Stabilizers	Ciba	B-225
PP (60 Melt Flow Index)	Various	PP 60MFI

Table 5

Mixing Equipment		Werner & Pfleiderer ZSK 25 co-rotating twin screw extruder					
Mixing Temperature		200°C					
Recipes and Order of Addition							
Recipe A	Recipe B	Recipe C	Recipe D	Recipe E	Recipe F (Comparative)	Recipe G	
Ingredient	Wt. %	Ingredient	Wt. %	Ingredient	Wt. %	Ingredient	Wt. %
I.44P Nanomer	12	I.44P Nanomer	12	I.44P Nanomer	12	I.44P Nanomer	12
Feeder 1 at Throat							
B-225	0.3	B-225	0.3	B-225	0.3	B-225	0.3
PB X5104	9	PB X5104	9	PB X5104	9	PB X5104	9
Profax 6323	18.7	Profax 6323	9.35	Profax 6323	38.7	Profax 6323	58.7
PP 60MFI	0	PP 60MFI	9.35	PP 60MFI	18.7	PP 60MFI	0
Feeder 2 at Throat							
Engage 8180	20	Engage 8180	20	Engage 8180	20	Engage 8180	20
Profax 6323	40	Profax 6323	40	Profax 6323	20	Profax 6323	50
Feeder 3 at Side Port Downstream							
Engage 8180	20	Engage 8180	20	Engage 8180	20	Engage 8180	20
Profax 6323	40	Profax 6323	40	Profax 6323	20	Profax 6323	50

Table 6

Example	Recipe Ratio*	Addition Parameters	Flexural Modulus ( $\pm$ Std. Dev.)		Modulus ( $\pm$ Std. Dev.)	Stress ( $\pm$ Std. Dev.)	% Elongation ( $\pm$ Std. Dev.)	Notched Izod ( $\pm$ Std. Dev.) with Break, if any.							
			ASTM D790 (psi*1000)	ASTM D638 (psi*1000)											
18A	40/60	500	40	302	$\pm$ 10	388	$\pm$ 21	4600	$\pm$ 200	7.2	$\pm$ 0.2	5.3	$\pm$ 0.5	Partial	
19A	40/60	1000	40	266	$\pm$ 2	355	$\pm$ 3	4330	$\pm$ 12	9.0	$\pm$ 0.1	10.3	$\pm$ 0.2	Partial	
20A	40/60	1000	80	263	$\pm$ 8	349	$\pm$ 5	4170	$\pm$ 22	7.8	$\pm$ 0.1	6.3	$\pm$ 0.5	Partial	
21A	40/60	500	80	228	$\pm$ 1	304	$\pm$ 5	3610	$\pm$ 29	7.3	$\pm$ 0.1	3.7	$\pm$ 0.2	Partial	
22B	40/60	500	80	272	$\pm$ 1	360	$\pm$ 7	4250	$\pm$ 8	8.3	$\pm$ 0.1	8.3	$\pm$ 0.4	Partial	
23B	40/60	1000	80	255	$\pm$ 4	347	$\pm$ 6	3890	$\pm$ 29	8.0	$\pm$ 0.3	6.9	$\pm$ 0.4	Partial	
24B	40/60	1000	40	232	$\pm$ 3	335	$\pm$ 12	4080	$\pm$ 2	8.1	$\pm$ 0.1	2.2	$\pm$ 0.2	Partial	
25B	40/60	500	40	254	$\pm$ 1	306	$\pm$ 7	3690	$\pm$ 6	7.8	$\pm$ 0.1	5.8	$\pm$ 0.1	Partial	
26C	40/60	1000	40	246	$\pm$ 2	344	$\pm$ 5	3870	$\pm$ 45	9.0	$\pm$ 0.3	12.0	$\pm$ 0.9	Non-break	
27C	40/60	500	80	231	$\pm$ 2	309	$\pm$ 12	3480	$\pm$ 61	7.2	$\pm$ 0.1	6.7	$\pm$ 0.4	Partial	
28D	60/40	500	40	280	$\pm$ 4	366	$\pm$ 12	4480	$\pm$ 30	7.8	$\pm$ 0.1	5.9	$\pm$ 0.4	Partial	
29D	60/40	1000	40	266	$\pm$ 4	346	$\pm$ 5	4300	$\pm$ 6	8.9	$\pm$ 0.1	6.9	$\pm$ 0.2	Partial	
30D	60/40	1000	80	241	$\pm$ 1	319	$\pm$ 7	3870	$\pm$ 15	8.3	$\pm$ 0.2	6.1	$\pm$ 0.3	Partial	
31D	60/40	500	80	222	$\pm$ 2	284	$\pm$ 6	3480	$\pm$ 7	7.8	$\pm$ 0.1	4.3	$\pm$ 0.3	Partial	
32E	60/40	1000	80	289	$\pm$ 3	378	$\pm$ 8	4480	$\pm$ 19	6.7	$\pm$ 0.1	4.5	$\pm$ 0.3	Partial	
33E	60/40	1000	40	257	$\pm$ 1	332	$\pm$ 5	3970	$\pm$ 9	7.8	$\pm$ 0.1	6.6	$\pm$ 0.3	Partial	
Comp. D	F	100/0	500	40	292	$\pm$ 2	383	$\pm$ 8	4500	$\pm$ 5	7.8	$\pm$ 0.2	7.0	$\pm$ 0.5	Partial
Comp. E	F	100/0	1000	40	243	$\pm$ 2	321	$\pm$ 9	3810	$\pm$ 13	9.6	$\pm$ 0.1	7.5	$\pm$ 0.4	Partial
Comp. F	F	100/0	1000	80	237	$\pm$ 1	313	$\pm$ 3	3720	$\pm$ 13	9.4	$\pm$ 0.2	6.7	$\pm$ 0.3	Partial
34G	30/70	1000	80	298	$\pm$ 1	390	$\pm$ 10	4470	$\pm$ 20	7.6	$\pm$ 0.1	7.2	$\pm$ 0.4	Partial	

\*Ratio of Addition of Ingredients at Throat vs. Downstream

Table 6 shows that addition of polyolefin elastomer at the side port downstream permits thorough dispersion of nanoclay, polypropylene, and maleated polypropylene in the extruder, such that an excellent performing TPO is made into pellets for subsequent molding or extrusion. The flexural modulus of the TPO is at least 222,000 lbs/in<sup>2</sup>. A direct comparison (Comparative Example D with Examples 18 and 28), (Comparative Example E with Examples 19 and 29), and (Comparative Example F with Examples 20, 30, and 34) shows higher flexural modulus with delayed addition of elastomer and delayed addition of a portion of the thermoplastic matrix polymer to improve ability to disperse nanoclay in the upstream section of the extruder.

Example 35

This example shows a 4:1 weight ratio of nanoclay to compatibilizing dispersion agent that has performance properties that do not require further dilution for extrusion-grade thermoplastic polyolefins. Table 7 shows the formulation. Table 8 shows the mechanical properties of the compound.

Table 7 Example 35 Formulation			
Ingredient and Use	Wt. Percent	Brand(s)	Source
Nanoclay to enhance stiffness	12	I44P	Nanocor
Polypropylene copolymer	84.2	Inspire 114	Dow
PP-g-MAH (maleated polypropylene) to disperse nanoclay	3	PolyBond PBX5104	Crompton
Di-stearyl-thio-dipropionate	0.5	DSTDTP	Various
Blend of Irganox 1010 and Irgafos 168 Processing Stabilizers	0.3	B-225	Ciba

Table 8		
Addition Parameters	Ratio	40/60
	Mix Speed (rpm)	1000
	Feed Rate (Lbs/hr)	80
Flexural Modulus ( $\pm$ Std. Dev.)	ASTM D790 (psi*1000)	323 $\pm$ 1
Modulus ( $\pm$ Std. Dev.)	ASTM D638 (psi*1000)	401 $\pm$ 7
Stress ( $\pm$ Std. Dev.)	ASTM D638 (psi)	4790 $\pm$ 14
% Elongation ( $\pm$ Std. Dev.)	ASTM D638 (in/in)	8.4 $\pm$ 0.2
Notched Izod ( $\pm$ Std. Dev.) with Break, if any	ASTM D256 (ft-lb/in)	5.9 $\pm$ 0.3 Partial Break

The invention is not limited to the above embodiments. The claims follow.

What is claimed is:

1. A method of making a nanocomposite of carrier, nanoclay, polyolefin elastomer and optional nanoclay dispersion agent, comprising the steps of
  - (a) adding the carrier, nanoclay, and optional nanoclay dispersion agent  
5 to an extruder; and
  - (b) adding the polyolefin elastomer downstream from where the carrier, nanoclay, and optional nanoclay dispersion agent were added.
- 10 2. A method of making a nanocomposite compound of thermoplastic matrix polymer, nanoclay, and compatibilizing dispersion agent, comprising the steps of:
  - (a) adding thermoplastic matrix polymer, nanoclay, compatibilizing dispersion agent as individual ingredients at an inlet of an extruder;
  - (b) adding polyolefin elastomer at a downstream port of the extruder.  
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- 15 3. The method of Claim 2, wherein step (a) also includes adding ingredients selected from the group consisting of colorants, nucleators, blowing agents, activators which lower the activation temperature of the blowing agent, surfactants, plasticizers, stabilizers, flame retardants, UV absorbers, fillers, 20 fragrances, mold release aids, processing aids, biocides, antistatic additives, anti-microbial agents, lubricants, and combinations of them.
4. A nanocomposite, comprising:  
thermoplastic matrix polymer, nanoclay, and compatibilizing dispersion  
25 agent having a weight ratio of nanoclay to compatibilizing dispersion agent of less than 2.2:1 and greater than 1:1.9.
- 30 5. The nanocomposite of Claim 4, wherein the nanocomposite further comprises a polyolefin elastomer.

6. The nanocomposite of Claim 4, wherein the nanoclay comprises at least 9 weight percent of the nanocomposite.

5       7. The nanocomposite of Claim 4, wherein the nanoclay comprises at least 10 weight percent of the nanocomposite.

8. The nanocomposite of Claim 4, wherein the nanoclay comprises at least 12 weight percent of the nanocomposite.

10       9. The nanocomposite of Claim 5, further comprising ingredients selected from the group consisting of colorants, nucleators, blowing agents, activators which lower the activation temperature of the blowing agent, surfactants, plasticizers, stabilizers, flame retardants, UV absorbers, fillers, fragrances, mold release aids, processing aids, biocides, antistatic additives, 15       anti-microbial agents, lubricants, and combinations of them.

10. A nanocomposite, comprising:  
thermoplastic matrix polymer, nanoclay, and compatibilizing dispersion agent having a weight ratio of nanoclay to compatibilizing dispersion agent of 20       greater than 3.1:1 and less than 10:1.

11. The nanocomposite of Claim 10, wherein the nanocomposite further comprises a polyolefin elastomer.

25       12. A method of using the nanocomposite of Claim 10, comprising the step of mixing the nanocomposite of Claim 10 with a thermoplastic polyolefin.

13. The method of Claim 12, wherein the mixing step occurs at a point of molding a final thermoplastic article.

14. The method of Claim 12, wherein the mixing step occurs at a ratio of about 4:1 of thermoplastic polyolefin to nanocomposite.

15. A method of using the nanocomposite of Claim 4, comprising the 5 step of pelletizing the nanocomposite of Claim 4 for further processing.

16. The method of Claim 15, wherein the further processing is molding or extruding the nanocomposite into a shape of an article.

10 17. The method of Claim 16, wherein the article is an auto part.

18. The method of Claim 16, wherein the article is a large appliance part.

15 19. An article made from the nanocomposite of Claim 4.

20. An article made from the nanocomposite of Claim 10 using the method of Claim 12.

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## Nanoclay-Containing Composites and Methods of Making Them

### Abstract

A composite of nanoclay and thermoplastic matrix polymer is disclosed, optionally containing a polyolefin elastomer and also optionally containing a dispersion agent for the nanoclay. The nanocomposite is prepared for use with thermoplastic polyolefins (TPO's). The polyolefin elastomer, preferably an ethylene-octene copolymer, is added into a mixing extruder downstream of the other ingredients. The nanoconcentrate contributes increased stiffness and toughness to a TPO, which can be used form molded articles such as automotive parts.

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